Activities of $\text{FeO}_{1.33}$ in the $\text{FeO}_x\text{--CaO--SiO}_2$ and $\text{FeO}_x\text{--CaO--SiO}_2\text{--Al}_2\text{O}_3$ Slags at 1 573 K Under Oxygen Partial Pressures between 10^{-6} and 10^{-2} atm

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(Received on February 2, 2016; accepted on March 17, 2016)

Qualities of sinters such as reducibility and strength are controlled by morphologies and mineral phases in iron ore sinters. Main mineral phases are hematite, magnetite and calcium ferrite. Slag phases are also included in sinters, which have been mainly liquid phases during the sintering process. Since iron ions in slags are hardly reduced to metallic irons in a blast furnace, iron oxides such as hematite and magnetite and calcium ferrite should be precipitated from molten slags during the sintering process. Precipitation of iron oxides and calcium ferrites from molten slags depends on the activity of FeO_x in molten slags from the thermodynamic view point. Therefore, the activities of $\text{FeO}_{1.33}$ have been measured over the wide ranges of chemical compositions in the single liquid phases of the $\text{FeO}_x\text{--CaO--SiO}_2$ and $\text{FeO}_x\text{--CaO--SiO}_2\text{--Al}_2\text{O}_3$ slags at 1 573 K under oxygen partial pressures between 10^{-6} and 10^{-2} atm. It has been found that the $a_{\text{FeO}_{1.33}}$ values have maximum at the $\text{CaO/SiO}_2(\text{mass}\%)$ ratios of 0.9–1.0 and 1.3–1.4 for the samples with 35 mass% FeO_x equilibrated at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and 1.0×10^{-4} atm, respectively. For the samples at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, on the other hand, $a_{\text{FeO}_{1.33}}$ monotonically increases with increasing the CaO/SiO_2 ratio within the compositional range of the single liquid region. As for the effect of the Al_2O_3 addition on the activities, the dependency of the activity on the CaO/SiO_2 ratio becomes moderate with increasing the Al_2O_3 addition on the sample at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm.

KEY WORDS: $\text{FeO}_x\text{--SiO}_2\text{--CaO}$ system; oxygen partial pressure; Al_2O_3 ; FeO_x activity.

1. Introduction

Qualities of sinters such as reducibility and strength are controlled by morphologies and mineral phases in iron ore sinters.¹⁾ Main mineral phases are hematite, magnetite and calcium ferrite. Volume fractions, sizes and shapes of these phases and concentrations of solid solutions in them are affected by many factors such as components and particle sizes of raw materials and sintering conditions.^{2–4)}

Silicate slag phases are also included in sinters, which have been mainly liquid phases during the sintering process. Molten slags play an important role as a binder of powdery raw materials of sinters during the sintering process. However, if excessive amount of molten slags are produced during the sintering process, large amount of slags remaining in sinters seriously reduces the strength of sinters. Presence of slags in sinters also causes a problem when the considerable amount of iron ions exists in the slag phases. Iron ions in slags are hardly reduced to metallic irons in a blast furnace because the rate of reducing agent supply into slags is substantially low. Therefore, iron oxide phases such as hematite and magnetite and calcium ferrite

should be precipitated from molten slags during the sintering process so as to suppress the production of slag phases in sinters. Precipitation of iron oxides and calcium ferrites from molten slags depends on the activity of FeO_x in molten slags from the thermodynamic view point. Therefore, it is of a great importance to know the variation with compositions of the FeO_x activities for designing of iron ore sinters. However, to the best of authors' knowledge, there are only few reports with respect to the FeO_x activities measured at the experimental conditions (temperatures and oxygen partial pressures in atmospheres) aiming for the development of iron ore sintering.

FeO activities in molten slags have been intensively measured at iron saturation on steelmaking slags.^{5–10)} In such experimental conditions, most iron ions exist as Fe^{2+} and the contents of Fe^{3+} in the slags are negligibly small. On the other hand, since the oxygen partial pressures in sintering processes are higher than those at iron saturation, the slags in sinters must contain higher Fe^{3+} contents than the slags at iron saturation, and the activities of iron oxides in the slags must be more strongly affected by the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$. Henao *et al.* have measured the activities of FeO and the activity coefficients of $\text{FeO}_{1.33}$ in the $\text{FeO}_x\text{--CaO--SiO}_2$ system at 1 573 K under intermediate oxygen partial pressures between two extremes of iron saturation

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DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-065>

and air atmosphere.¹¹⁾ However, they have only measured the activities in the limited compositional areas. The present authors have previously determined the compositional areas of the single liquid phases in the $\text{FeO}_x\text{--CaO--SiO}_2$ and the $\text{FeO}_x\text{--CaO--SiO}_2\text{--Al}_2\text{O}_3$ systems at 1 573 K at three different oxygen partial pressures of 10^{-6} , 10^{-4} and 10^{-2} atm, and have found that the areas of the single liquid phases are much larger than the areas for which Henao *et al.* have measured the activities.¹²⁾ Therefore, the aim of this study is to measure the activities of $\text{FeO}_{1.33}$ over the wider ranges of chemical compositions in the single liquid phases at 1 573 K under oxygen partial pressures between 10^{-6} and 10^{-2} atm so as to clarify the effect of the slag compositions on the activities.

2. Experimental

2.1. Equilibrium Experiments

Three series of samples were prepared:

Series 1: $35(\text{mass}\%)\text{Fe}_2\text{O}_3\text{--}65a\text{CaO--}65(1-a)\text{SiO}_2$

$a/(1-a) = 0.5, 0.65, 1, 1.2, 1.35, 1.5$, and 1.87

Series 2: $b(\text{mass}\%)\text{Fe}_2\text{O}_3\text{--}0.48(100-b)\text{CaO--}0.52(100-b)\text{SiO}_2$

$b = 20, 35, 40, 60$, and 80

Series 3: $35(\text{mass}\%)\text{Fe}_2\text{O}_3\text{--}(65-c)d\text{CaO--}(65-c)(1-d)\text{SiO}_2\text{--}c\text{Al}_2\text{O}_3$

$c = 2$ or 5 , and $d/(1-d) = 0.5, 0.65, 1$, and 1.2

Samples were prepared from reagent grade Fe_2O_3 , SiO_2 , Al_2O_3 and CaCO_3 powders, the last being decomposed to CaO by heating at 1 373 K for 12 h in air. The reagents were weighed to the desired compositions and mixed in an alumina mortar. About 0.4 g of these mixtures were contained in a Pt crucible which was folded from Pt foil (12 mm $\times$ 35 mm and 0.02 mm in thickness), then suspended by a Pt wire within the uniform temperature region of a SiC resistance furnace. Experiments were carried out in air or in a flow of Ar--O_2 gases (50 ml/min.). Oxygen partial pressures in the Ar--O_2 gases were confirmed using an oxygen sensor to be 2.5×10^{-6} atm, 1.0×10^{-4} atm and 1.0×10^{-2} atm. The temperature at a uniform temperature region was controlled within $1\,573 \pm 2$ K. In accordance with the preliminary experiment described in the section 2.2, the heating durations of the samples were set to be 72 h, which is long enough for the samples to be thermodynamically equilibrated with the gas phase as well as the Pt foil. The samples held at 1 573 K were quenched into iced water. The phases of the samples were determined by X-ray diffraction (XRD) analyses. The chemical compositions of liquid phases were measured by an electron probe microanalyzer (EPMA) with an accelerating voltage of 15 kV and a probe current of 20 nA. A homogeneous glassy sample having the composition of 24.58 mass%Fe, 25.53 mass%Ca, 12.84 mass%Si, 1.06 mass%Al and 35.98 mass%O was used as a standard sample for quantitative analyses by EPMA. The composition of the standard sample was calculated using the mixture fractions of the Fe_2O_3 , CaO , SiO_2 and Al_2O_3 powders and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio analyzed by Mössbauer spectroscopy. The compositions of the samples were repeatedly-analyzed at different five positions in the cross-sectional areas. The errors were within $\pm 2\%$.

2.2. Calculation Methodology of the Activity of $\text{FeO}_{1.33}$

The $\text{FeO}_{1.33}$ activities in the slag samples are estimated based on the following chemical reaction,

Here, a slag sample is assumed to be in equilibrium with the gas atmosphere of known oxygen partial pressure and the Pt crucible containing Fe. Namely, Fe content in the Pt crucible is assumed to be controlled by Eq. (1). The standard Gibbs energy of the formation of solid $\text{FeO}_{1.33}$, ΔG^0 , is written as¹³⁾

$$\Delta G^0 / \text{Jmol}^{-1} = -367\,414 + 102.47T = -RT \ln \frac{a_{\text{FeO}_{1.33}}}{a_{\text{Fe}} P_{\text{O}_2}^{2/3}} \quad \dots\dots (2)$$

where T , $a_{\text{FeO}_{1.33}}$, a_{Fe} and P_{O_2} represent the temperature, the activity of $\text{FeO}_{1.33}$, the activity of Fe and the oxygen partial pressure, respectively. The standard states of $a_{\text{FeO}_{1.33}}$ and a_{Fe} are taken as solid $\text{FeO}_{1.33}$ and pure solid iron at the experimental temperature, respectively. The values of $a_{\text{FeO}_{1.33}}$ can be unambiguously determined when the slag is in the equilibrium state. From Eq. (2), the $a_{\text{FeO}_{1.33}}$ values in the samples can be calculated using the a_{Fe} values in the Pt foil and the P_{O_2} values in the gas phase. The a_{Fe} values in the Pt foil were obtained by the method described in the section 2.4. The P_{O_2} values in the gas phase were measured by an oxygen sensor as aforementioned.

2.3. Measurement of Fe Contents in Pt Foils in Equilibrium with Slags

Figure 1 shows a back-scattered electron (BSE) image of a sample heated for 24 h (a), the line profile of the Fe element for the same sample (b), and the line profile of the Fe element for the sample heated for 72 h (c). In the samples, the equilibrated phases consist of a liquid phase and magnetite. The area with "B.G." corresponds to the resin used for the sample preparation for the EPMA observation. It can be seen from Fig. 1(b) that the Fe distribution across the thickness of the Pt foil is uniform, demonstrating that the equilibrium could be attained in 24 h. The Fe content in the Pt foil was calculated by comparing the X-ray intensity in the Pt foil and that in the slag (liquid phase) after the background intensity was subtracted from both. Here, the Fe content in the slag was preliminarily analyzed by spot analyses as aforementioned in the section 2.1. It has been found that the Fe contents in the Pt foils of the samples heated for 24 h and 72 h are identical within the analytical errors. This also supports that the equilibrium could be attained in 24 h. On the other hand, one of the present authors have reported that the time demanded for the coordination structures of iron ions to settle down at the equilibrium state is about three times as long as that for the valence states of iron ions in the same slags.¹⁴⁾ Therefore, the authors have adopted 72 h as the heating duration in this study.

2.4. Determination of Fe Activities in Pt Foils in Equilibrium with Slags

a_{Fe} was obtained by multiplying the Fe content ($= N_{\text{Fe}}$) in the Pt foil by the activity coefficient of Fe ($= \gamma_{\text{Fe}}$) in the Fe–Pt alloy. N_{Fe} was measured in the same manner as described in the section 2.3. The γ_{Fe} values of Fe–Pt alloys have been investigated by several authors. The experimental

data available in the literatures were carefully compared by Fredriksson and Seetharaman.¹⁵⁾ The discrepancies can be recognized particularly in the lower Fe concentrations. Therefore, the γ_{Fe} values were also measured in this study.

The γ_{Fe} values can be experimentally obtained by measuring the N_{Fe} values in the Pt foil equilibrated with the slags composed of magnetite and a liquid phase at known oxygen partial pressures because the CaO and SiO₂ solid solutions in magnetite are negligible.¹²⁾ Magnetite is thermodynamically stable at oxygen partial pressures of 2.5×10^{-6} atm, 1.0×10^{-4} atm and 1.0×10^{-2} atm. According to the Fe–O phase diagram,¹⁶⁾ magnetite is a nonstoichiometric compound, deviating from the stoichiometric compound of Fe₃O₄ toward the O-rich compositional region. The atomic ratios of O/Fe in magnetite have been reported by Phillips and Muan¹⁷⁾ as functions of temperature and oxygen partial pressure, where the O/Fe ratios ($= x$) in magnetite, FeO_{*x*}, at 1 573 K are found to be 1.337, 1.339 and 1.346 at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, 1.0×10^{-4} atm and 1.0×10^{-2} atm,

respectively. Spencer and Kubaschewski have reported the standard Gibbs energy of formation of nonstoichiometric magnetite, ΔG_f^0 , as a function of the Fe/O ratio.¹⁸⁾ The ΔG_f^0 values at 1 573 K can be estimated to be -206.68 kJ/mol, -206.59 kJ/mol and -206.31 kJ/mol at $x = 1.337$, 1.339 and 1.346, respectively. Therefore, the γ_{Fe} values in Pt can be calculated using the following equation.

$$\text{Fe} + \frac{x}{2} \text{O}_2 = \text{FeO}_x \quad \Delta G_f^0 = -RT \ln \frac{a_{\text{FeO}_x}}{\gamma_{\text{Fe}} N_{\text{Fe}} P_{\text{O}_2}^{x/2}} \dots\dots\dots (3)$$

where the activity of FeO_{*x*}, a_{FeO_x} , is unity for the slags in equilibrium with FeO_{*x*}.

3. Results

Tables 1 through **3** show the compositions of either single liquid phase or a liquidus phase in equilibrium with solid magnetite, 2CaO·SiO₂ (hereinafter denoted as C2S) or CaO·SiO₂ (hereinafter denoted as CS). The FeO_{*x*} contents

Fig. 1. A back-scattered electron (BSE) image of a sample heated for 24 h (a), the line profile of the Fe element for the same sample (b), and the line profile of the Fe element for the sample heated for 72 h (c).

Table 1. Equilibrated liquidus compositions and $a_{\text{FeO}1.33}$ values at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm and mass%Al₂O₃ = 0 (a) and at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm and mass%Al₂O₃ > 0 (b).

(a)												
Series	No.	P _{O2} (atm)	Phase	compositions of liquidus phase (mass%)				C/S	Heating duration (hours)	N _{Fe} in Pt (mol%)	log γ _{Fe}	log <i>a</i> _{FeO1.33}
				FeO _x	CaO	SiO ₂	Al ₂ O ₃					
1	A01	2.5×10 ^{−6}	Liq.	31.55	34.95	33.50	0.00	1.04	72	0.092	−3.644	−1.564
2	A06	2.5×10 ^{−6}	Liq.	38.42	30.76	30.83	0.00	1.00	72	0.126	−3.085	−0.871
1	A08	2.5×10 ^{−6}	Liq.	30.09	37.52	32.39	0.00	1.16	72	0.121	−3.155	−0.957
1	A10	2.5×10 ^{−6}	Liq.	27.09	30.11	42.80	0.00	0.70	72	0.084	−3.795	−1.757
1	A19	2.5×10 ^{−6}	Liq.	38.23	21.70	40.07	0.00	0.54	72	0.086	−3.766	−1.720
2	A02	2.5×10 ^{−6}	Liq. + Magnetite	41.04	30.67	28.29	0.00	1.08	72	0.178	−2.371	−0.006
2	A09	2.5×10 ^{−6}	Liq. + CS	21.62	41.63	36.76	0.00	1.13	72	0.074	−3.973	−1.988
1	A07	2.5×10 ^{−6}	Liq.+ C2S	40.15	35.98	23.87	0.00	1.51	72	0.112	−3.313	−1.151
(b)												
Series	No.	P _{O2} (atm)	Phase	compositions of liquidus phase (mass%)				C/S	Heating duration (hours)	N _{Fe} in Pt (mol%)	log γ _{Fe}	log <i>a</i> _{FeO1.33}
				FeO _x	CaO	SiO ₂	Al ₂ O ₃					
3	A15	2.5×10 ^{−6}	Liq.	36.75	25.00	36.34	1.91	0.69	72	0.073	−3.993	−2.013
3	A17	2.5×10 ^{−6}	Liq.	36.30	34.51	27.58	1.61	1.25	72	0.086	−3.753	−1.704
3	A16	2.5×10 ^{−6}	Liq.	36.04	24.07	35.17	4.72	0.68	72	0.061	−4.229	−2.328
3	A18	2.5×10 ^{−6}	Liq.	36.08	32.83	26.55	4.55	1.24	72	0.074	−3.977	−1.993
3	A20	2.5×10 ^{−6}	Liq.	36.70	19.62	37.48	6.19	0.52	72	0.089	−3.706	−1.644

Table 2. Equilibrated liquidus compositions and $a_{\text{FeO}1.33}$ values at $P_{\text{O}_2} = 1.0 \times 10^{-4}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 = 0$ (a) and at $P_{\text{O}_2} = 1.0 \times 10^{-4}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 > 0$ (b).

(a)												
Series	No.	P_{O_2} (atm)	Phase	compositions of liquidus phase (mass%)				C/S	Heating duration (hours)	N_{Fe} in Pt (mol%)	$\log \gamma_{\text{Fe}}$	$\log a_{\text{FeO}1.33}$
				FeO _x	CaO	SiO ₂	Al ₂ O ₃					
1	C05	1.0×10^{-4}	Liq.	32.09	40.86	27.05	0.00	1.51	72	0.082	-3.829	-0.734
1	C06	1.0×10^{-4}	Liq.	29.36	38.43	32.21	0.00	1.19	72	0.085	-3.778	-0.669
1	C07	1.0×10^{-4}	Liq.	30.48	28.12	41.40	0.00	0.68	72	0.061	-4.238	-1.274
2	C10	1.0×10^{-4}	Liq.	34.11	30.09	35.80	0.00	0.84	72	0.060	-4.245	-1.283
1	C21	1.0×10^{-4}	Liq.	34.50	22.03	43.47	0.00	0.51	72	0.059	-4.273	-1.321
2	C26	1.0×10^{-4}	Liq.	41.76	29.98	28.26	0.00	1.06	72	0.092	-3.652	-0.508
2	C25	1.0×10^{-4}	Liq. + Magnetite	46.60	25.28	28.11	0.00	0.90	72	0.117	-3.224	0.025
2	C11	1.0×10^{-4}	Liq. + CS	29.28	32.31	38.41	0.00	0.84	72	0.053	-4.397	-1.492
(b)												
Series	No.	P_{O_2} (atm)	Phase	compositions of liquidus phase (mass%)				C/S	Heating duration (hours)	N_{Fe} in Pt (mol%)	$\log \gamma_{\text{Fe}}$	$\log a_{\text{FeO}1.33}$
				FeO _x	CaO	SiO ₂	Al ₂ O ₃					
3	C13	1.0×10^{-4}	Liq.	32.39	32.52	32.76	2.33	0.99	72	0.062	-4.215	-1.243
3	C15	1.0×10^{-4}	Liq.	35.18	25.24	37.06	2.53	0.68	72	0.061	-4.243	-1.280
3	C17	1.0×10^{-4}	Liq.	37.29	34.89	25.68	2.14	1.36	72	0.077	-3.928	-0.862
3	C16	1.0×10^{-4}	Liq.	34.56	24.95	35.00	5.49	0.71	72	0.052	-4.410	-1.511
3	C14	1.0×10^{-4}	Liq.	33.98	30.82	29.28	5.92	1.05	72	0.056	-4.330	-1.400
3	C18	1.0×10^{-4}	Liq.	36.89	33.54	24.83	4.75	1.35	72	0.076	-3.944	-0.883

Table 3. (a) Equilibrated liquidus compositions and $a_{\text{FeO}1.33}$ values at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 = 0$ (a) and at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 > 0$ (b).

(a)												
Series	No.	P_{O_2} (atm)	Phase	compositions of liquidus phase (mass%)				C/S	Heating duration (hours)	N_{Fe} in Pt (mol%)	$\log \gamma_{\text{Fe}}$	$\log a_{\text{FeO}1.33}$
				FeO _x	CaO	SiO ₂	Al ₂ O ₃					
2	B01	1.0×10^{-2}	Liq.	38.55	31.53	29.92	0.00	1.05	72	0.057	-4.316	-0.049
2	B04	1.0×10^{-2}	Liq.	29.72	33.30	36.98	0.00	0.90	72	0.045	-4.567	-0.405
1	B06	1.0×10^{-2}	Liq.	32.63	35.91	31.46	0.00	1.14	72	0.050	-4.453	-0.241
1	B07	1.0×10^{-2}	Liq.	34.51	23.85	41.64	0.00	0.57	72	0.050	-4.461	-0.252
1	B09	1.0×10^{-2}	Liq.	34.56	24.14	41.30	0.00	0.58	72	0.053	-4.401	-0.168
1	B10	1.0×10^{-2}	Liq.	34.49	39.02	26.49	0.00	1.47	72	0.046	-4.547	-0.375
2	B11	1.0×10^{-2}	Liq.	37.93	31.95	30.12	0.00	1.06	72	0.052	-4.417	-0.190
1	B12	1.0×10^{-2}	Liq.	34.60	38.76	26.63	0.00	1.46	72	0.046	-4.535	-0.358
1	B21	1.0×10^{-2}	Liq.	36.30	20.27	43.43	0.00	0.47	72	0.048	-4.505	-0.315
2	B02	1.0×10^{-2}	Liq. + Magnetite	46.50	26.57	26.93	0.00	0.99	72	0.058	-4.300	-0.027
2	B08	1.0×10^{-2}	Liq. + Magnetite	43.81	27.17	29.02	0.00	0.94	72	0.058	-4.301	-0.029
2	B23	1.0×10^{-2}	Liq. + Magnetite	42.20	29.71	28.09	0.00	1.06	24	0.058	-4.300	-0.028
2	B03	1.0×10^{-2}	Liq. + CS	25.21	32.16	42.63	0.00	0.75	72	0.030	-4.876	-0.881
(b)												
Series	No.	P_{O_2} (atm)	Phase	compositions of liquidus phase (mass%)				C/S	Heating duration (hours)	N_{Fe} in Pt (mol%)	$\log \gamma_{\text{Fe}}$	$\log a_{\text{FeO}1.33}$
				FeO _x	CaO	SiO ₂	Al ₂ O ₃					
3	B13	1.0×10^{-2}	Liq.	36.10	32.70	28.90	2.29	1.13	72	0.052	-4.422	-0.197
3	B15	1.0×10^{-2}	Liq.	36.14	25.74	35.87	2.25	0.72	72	0.054	-4.381	-0.139
3	B17	1.0×10^{-2}	Liq.	35.18	35.48	27.29	2.05	1.30	72	0.051	-4.429	-0.207
3	B14	1.0×10^{-2}	Liq.	35.09	30.67	28.39	5.86	1.08	72	0.049	-4.469	-0.263
3	B16	1.0×10^{-2}	Liq.	34.57	24.40	36.05	4.99	0.68	72	0.052	-4.412	-0.183
3	B18	1.0×10^{-2}	Liq.	39.69	29.91	25.22	5.18	1.19	72	0.050	-4.464	-0.257
3	B22	1.0×10^{-2}	Liq.	39.84	17.40	38.44	4.32	0.45	72	0.056	-4.335	-0.076

have been calculated by considering FeO_x as FeO.

Figure 2 shows the relation between the γ_{Fe} and N_{Fe} (mol%) values at 1 573 K. The previous data^{11,19)} are also

included in Fig. 2, where the γ_{Fe} values by Henao *et al.*¹¹⁾ have been re-calculated by the present authors using their tabulated raw data of Fe concentrations in Pt crucibles. The

values reported by Henao *et al.*¹¹⁾ are in good agreement with the present data. However, the values by Tayler *et al.*¹⁹⁾ do not accord with the others at lower N_{Fe} values. Tayler *et al.*¹⁹⁾ observed the weight change of a pellet prepared by sintering Fe_2O_3 and platinum mixtures by thermogravimetry while reducing the oxygen pressure from the air atmosphere ($P_{\text{O}_2} = 0.21$ atm) to the desired pressure, so that the Fe concentrations in Pt can be estimated assuming that the Fe/Pt atomic ratio is constant during the heating experiment. In their method, the accuracy of the measured N_{Fe} values may be worse at lower Fe concentrations owing to the smaller weight change. Therefore, the relation between the γ_{Fe} and N_{Fe} (mol%) values have been determined using the present data at the N_{Fe} values lower than 0.18 as follows:

$$\log \gamma_{\text{Fe}} = -34.589N_{\text{Fe}}^2 + 24.162N_{\text{Fe}} - 5.5796 \dots (4)$$

This equation has been subjected to the derivation of the

Fig. 2. Relation between the γ_{Fe} and N_{Fe} (mol%) values at 1573 K.

Fig. 3. Activities of $\text{FeO}_{1.33}$ at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 = 0$ (a) and at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 > 0$ (b).

activities in this study.

Figures 3 through 5 show the activities of $\text{FeO}_{1.33}$, $a_{\text{FeO}_{1.33}}$, on the $\text{FeO}_x\text{--CaO--SiO}_2$ slags with and without Al_2O_3 at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, 1.0×10^{-4} atm and 1.0×10^{-2} atm, respectively. The standard state of the activities is taken as the stoichiometric solid $\text{FeO}_{1.33}$. The data of slags equilibrated with a solid phase of either magnetite, CS or C2S are

Fig. 4. Activities of $\text{FeO}_{1.33}$ at $P_{\text{O}_2} = 1.0 \times 10^{-4}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 = 0$ (a) and at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 > 0$ (b).

Fig. 5. Activities of $\text{FeO}_{1.33}$ at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 = 0$ (a) and at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm and $\text{mass}\% \text{Al}_2\text{O}_3 > 0$ (b).

plotted at the compositions of the liquidus phase. The numbers in the figures correspond to the logarithm of $a_{\text{FeO}1.33}$.

4. Discussion

4.1. Relation between $a_{\text{FeO}1.33}$ Values and FeO_x Concentrations

Figure 6 shows the relations between the $a_{\text{FeO}1.33}$ values and the FeO_x concentrations for the samples having a single liquid phase with the CaO/SiO_2 (mass%) ratio of 0.93 (Series 2), which is equivalent to the CaO/SiO_2 (mol%) ratio of unity, at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, 1.0×10^{-4} atm and 1.0×10^{-2} atm. It has been found that the samples with 20 mass% Fe_2O_3 in Series 2 equilibrated at all the experimental oxygen partial pressures contain CS as well as a liquid phase, and those with 60 and 80 mass% Fe_2O_3 in Series 2 magnetite together with a liquid phase. Figure 6 also includes the line denoted as “ideal solution” obeying the linear variation of $a_{\text{FeO}1.33}$ with respect to molar fraction of FeO_x below the liquidus line in equilibrium with magnetite at $P_{\text{O}_2} = 1.0 \times 10^{-4}$ atm. The measured $a_{\text{FeO}1.33}$ values exhibit negative deviation from the ideal solution line, which implies that the Fe ions are located in the stable states by taking a specific structure rather than the random structure.

4.2. Relation between $a_{\text{FeO}1.33}$ Values and CaO/SiO_2 Ratios

Figure 7 shows the $a_{\text{FeO}1.33}$ values for the samples with 35 mass% FeO_x (Series 1) as a function of the CaO/SiO_2 (mass%) ratio. The samples were equilibrated at either $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, 1.0×10^{-4} atm or 1.0×10^{-2} atm. It has been found that the sample with the CaO/SiO_2 (mass%) ratio of 1.87 at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm does not consist of a single liquid phase, but includes C2S with a liquid phase. Therefore, the result was omitted from Fig. 7. The $a_{\text{FeO}1.33}$ values have peaks at the CaO/SiO_2 (mass%) ratios of 0.9–1.0 and 1.3–1.4 for the samples equilibrated at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and 1.0×10^{-4} atm, respectively. For the samples at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, on the other hand, the $a_{\text{FeO}1.33}$ value monotonically increases with increasing the CaO/SiO_2 ratio within the compositional range of the single liquid

Fig. 6. Activity of $\text{FeO}_{1.33}$ in the FeO_x – CaO – SiO_2 system at the CaO/SiO_2 (mass%) ratio of 0.93, which is equivalent to the CaO/SiO_2 (mol%) ratio of unity, as a function of the FeO_x concentrations. The line denoted as “ideal solution” is the linear variation of $a_{\text{FeO}1.33}$ with respect to molar fraction of FeO_x below the liquidus line in equilibrium with magnetite at $P_{\text{O}_2} = 1.0 \times 10^{-4}$ atm.

region. As for the effect of the slag basicity on the iron oxide activity, Sano⁹⁾ has measured the FeO activities in the FeO_x – Na_2O – SiO_2 slags at iron saturation, and has suggested that the iso-activity contour have the noses at the $\text{Na}_2\text{O}/\text{SiO}_2$ (mol%) ratio of unity based on his data as well as the Richardson’s model.²⁰⁾ He has also explained using the same model that the iso-activity contours for FeO in the FeO_x – CaO – SiO_2 slags at iron saturation have the noses at the line joining the compositions FeO and C2S . In fact, C2S is known to be the most stable intermediate compound in the CaO – SiO_2 binary system. Therefore, it is considered that as the CaO/SiO_2 (mol%) ratio approaches to two, the affinity of FeO_x with matrix CaO – SiO_2 in the FeO_x – CaO – SiO_2 system could become less, resulting in the higher activity of FeO_x . This consideration is consistent with the monotonical increase in the $a_{\text{FeO}1.33}$ values with the CaO/SiO_2 ratio for the sample at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, as shown in Fig. 7. However, the variation of the $a_{\text{FeO}1.33}$ values exhibit maximum in the CaO/SiO_2 ratio lower than two for the samples at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and 1.0×10^{-4} atm. This may be relevant to the increase in the ratio of Fe^{3+} to the total iron ions in the slags. Fe^{3+} ions are incorporated in the matrix CaO – SiO_2 , polymerizing the silicate network structure.²¹⁾ As a consequence, Fe^{3+} ions may suppress the tendency that the activity of FeO_x is dominated by the CaO/SiO_2 ratio.

Figures 8 and 9 show the effects of Al_2O_3 addition on the relation between the $a_{\text{FeO}1.33}$ values and the CaO/SiO_2 (mass%) ratios for the samples of Series 3 equilibrated at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ and 1.0×10^{-2} atm, respectively. It can

Fig. 7. Activity of $\text{FeO}_{1.33}$ in the 35(mass%) FeO_x – CaO – SiO_2 slags (Series 1) as a function of the CaO/SiO_2 (mass%) ratio.

Fig. 8. Effect of Al_2O_3 addition on the relation between the $\text{FeO}_{1.33}$ activities and the CaO/SiO_2 (mass%) ratio for the samples equilibrated at $P_{\text{O}_2} = 2.5 \times 10^{-6}$.

Fig. 9. Effect of Al_2O_3 addition on the relation between the $\text{FeO}_{1.33}$ activities and the CaO/SiO_2 (mass%) ratio for the samples equilibrated at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm.

be seen that the dependency of the activity on the CaO/SiO_2 ratio becomes moderate with increasing the Al_2O_3 addition on the sample at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm although the variation of the activity with the CaO/SiO_2 ratio is identical irrespective of the Al_2O_3 addition on the sample at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm. Al_2O_3 addition may play the same role as Fe^{3+} ions on the $a_{\text{FeO}_{1.33}}$ values: Al_2O_3 addition polymerizes the silicate network structure. Therefore, the Al_2O_3 addition may weaken the C2S formation effect on the affinity of FeO_x with the matrix silicates.

5. Conclusions

The activities of $\text{FeO}_{1.33}$ in the single liquid phases of the $\text{FeO}_x\text{--CaO--SiO}_2$ and the $\text{FeO}_x\text{--CaO--SiO}_2\text{--Al}_2\text{O}_3$ systems have been measured at 1 573 K under oxygen partial pressures between 10^{-6} and 10^{-2} atm so as to clarify the effect of the slag compositions on the activities. The obtained results are summarized as follows.

(1) The obtained relations between the $a_{\text{FeO}_{1.33}}$ values and the FeO_x concentrations for the samples having a single liquid phase with the CaO/SiO_2 (mol%) ratios of unity indicate that the $a_{\text{FeO}_{1.33}}$ values exhibit negative deviation from the ideal solution model. This implies that the Fe ions are located in the stable states by taking a specific structure rather than the random structure.

(2) It can be seen from the relation between the $a_{\text{FeO}_{1.33}}$ values and the CaO/SiO_2 ratios for the samples with 35 mass% FeO_x that the $a_{\text{FeO}_{1.33}}$ values have peaks at the CaO/SiO_2 (mass%) ratios of 0.9–1.0 and 1.3–1.4 at $P_{\text{O}_2} = 1.0 \times 10^{-2}$ atm and 1.0×10^{-4} atm, respectively. For the samples at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm, on the other hand, the $a_{\text{FeO}_{1.33}}$ value monotonically increases with increasing the CaO/SiO_2 ratio within the compositional range of the single liquid region. The CaO/SiO_2 ratio at the maximum of the $a_{\text{FeO}_{1.33}}$ value may be dependent on the ratio of Fe^{3+} to the total iron ions in the slags: Fe^{3+} ions are incorporated in the matrix CaO--SiO_2 , polymerizing the silicate network structure. As a consequence, Fe^{3+} ions may suppress the tendency that the activity of FeO_x is dominated by the CaO/SiO_2 ratio.

(3) The dependency of the $\text{FeO}_{1.33}$ activities on the CaO/SiO_2 ratio becomes moderate with increasing the Al_2O_3 addition on the sample at $P_{\text{O}_2} = 2.5 \times 10^{-6}$ atm. This could be because Al_2O_3 addition may play the same role as Fe^{3+} ions on the silicate network structures.

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